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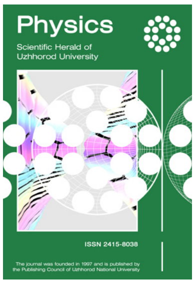

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Theoretical Aspects of Hydrogen Diffusion in Metals

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Abstract

Relevance. The diffusion of hydrogen in metals has received a lot of attention and has been the subject of intensive training in recent decades, this is due to the practical interest in using the metal-hydrogen system for a number of technological applications, including the creation of radiation-resistant materials and filters for producing pure hydrogen, for using gas H as a secondary energy carrier, and fusion reactor technology. H diffusion in Fe alloys is very important because this leads to engineering problems associated with hydrogen embrittlement and degradation of high strength steels, reactor materials, etc.

Purpose. The aim of the present work is to study the mechanism of hydrogen atom diffusion in the crystal lattice of metals using the statistical thermodynamics method and to calculate the extended diffusion equation and the pre-exponential factor for the corresponding Arrhenius equation.

Methods. The propose to use statistical model expressions the pre-exponential factor and the jump frequency for a more accurate calculation of the hydrogen diffusion in molecular dynamics (MD) and centroid path-integral molecular dynamics (CMD).

Results. Our approach based on the first principles of a statistical model makes it possible coherently describing the temperature dependence of the diffusion coefficient H in $\boldsymbol{\alpha}$-Fe in a wide temperature range from 100 to 1000 K. The values of the activation energy and the pre-exponential factor of the over-barrier diffusion of hydrogen in α-Fe, Pd, Ag, Al, Ni and γ-Fe, obtained in the present work, are good consistent with the experimental data.

Conclusions. The results show that statistical effects play a decisive role in the H migration process both at ambient temperature and at higher temperatures. The statistical model makes it possible to explain the high values of the pre-exponential diffusion factor at high temperatures due to the T^2 coefficient

Keywords: statistical model, hydrogen diffusion, pre-exponential factor, molecular dynamics; activation energy, jump frequency

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Introduction

The diffusion of hydrogen in metals has received a lot of attention and has been the subject of intensive training in recent decades. First, this is due to the practical interest in using the metal – hydrogen system for a number of technological applications, including the creation of radiation-resistant materials and filters for producing pure hydrogen, for using gas H as a secondary energy carrier, and fusion reactor technology [1; 2]. Secondly, it is caused by the undesirable effect of hydrogen on the properties of materials (embrittlement, corrosion, crack propagation) [3; 4]. In particular, H diffusion in Fe and Fe alloys is very important because this leads to engineering problems associated with hydrogen embrittlement and degradation of high strength steels, reactor materials, etc. [5; 6].

Hydrogen atoms have a unique low mass and size in comparison with other interstitial atoms in metals, and for this reason they have an extremely high diffusion mobility [7-9]. The diffusion coefficients of hydrogen in solid metals are almost the same as in liquids. This function, in addition to the small size and mass of the hydrogen atom, is also associated with the dissociation of the hydrogen molecule into individual atoms when it enters the metal [9; 10]. In metal crystals, hydrogen atoms are in interstitials and in the diffusion process they pass from one interstitial site to another. In FCC lattice, hydrogen can occupy two types of interstitial sites: octahedral and tetrahedral. At the present time, the question of the mechanism of hydrogen diffusion in the crystal lattice of metals remains. Even in a pure crystal, transitions between interstitials of different types are possible, which entails, in particular, the ambiguity of the activation energy of hydrogen diffusion. In addition, as noted in [7], the redistribution of hydrogen atoms in interstitial sites of various types due to changes in external conditions, for example, deformation, can lead to a change in the diffusion parameters. It should be noted that other factors may also lead to deviations from the Arrhenius law, in particular, the possibility of diffusion jumps of different lengths and the effect of crystal lattice defects [1; 5]. This high diffusion mobility is thought to be the result of a very low activation energy due to the quantum nature of H [11].

Although there has been a significant amount of experimental research on the diffusion of hydrogen [12-15], very little reliable data available, especially on the distribution at temperatures below room temperature. First principles calculations and classical approaches molecular mechanics has been used to study hydrogen adsorption, absorption, dissolution and diffusion energy in the case of body-centered cubic (bcc) Fe in several papers [16-20]. It is assumed that modern ab initio modeling will provide a good description of the geometry, energy, and potential energy surface in Fe-H systems. However, as far as we know, there is no systematic derivation of the diffusion coefficients for which quantum-statistical effects are taken into account in a wide temperature range [11]. The use of such calculations is important for understanding the possible mechanisms of hydrogen diffusion in metalls.

The aim of the present work is to study the mechanism of hydrogen atom diffusion in the crystal lattice of metals using the statistical thermodynamics method and to calculate the extended diffusion equation and the pre-exponential factor in the corresponding Arrhenius equation.

Teoretical Framework

The classical atomic theory of diffusion gives an expression for the diffusion coefficient self-diffusion. In early works on the statistical theory Ya.I. Frenkel and his followers, the dependence of the diffusion coefficient on the square of the distance between two atomic positions was obtained [21-24]. This expression for the diffusion coefficient is also commonly used in modern molecular dynamics [11; 25]. However, due to a significant discrepancy between the calculated and experimental data, even in these classical works, additional parameters were introduced to calculate the diffusion coefficients. At the same time, it is well known, that the main driving forces of diffusion in non-equilibrium thermodynamics are the gradients of chemical potentials μ_i of the components of the system [24; 26]. This position should be taken into account when deriving equations for the diffusion coefficient. However, it is very difficult to introduce chemical potentials into the diffusion equations in the atomic statistical model.

In solid state physics for the analysis of multicomponent systems – solid solutions, etc. – long and widely used methods of statistical physics [26; 27], in particular, thermodynamics. In statistical thermodynamics, equations describing thermionic emission have long been known [26; 27]. To describe the diffusion of atoms in the crystal lattice of a metal in work [28] was developed the statistical model, previously well used for the description of thermionic emission. Large attractive forces hold atoms in the crystal lattice of a metal; therefore, the potential energy of moving, i.e. diffusing atoms is greater than the potential energy of the atoms of the crystal lattice by the value of U – the activation energy of the diffusion process. Was can select out in a unit volume of metal V a unit surface perpendicular to the x axis (Fig. 1):

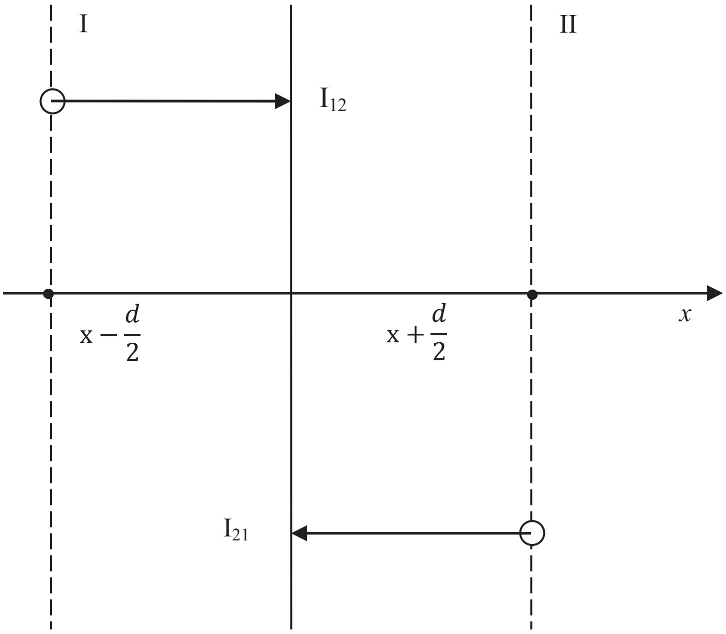

Figure 1. Scheme of diffusion in the statistical atomic model

Source: [24; 28]

The total flux of diffusing atoms in the positive direction of the *x*-axis is equal to the difference in the flux I_{12} (from the plane $x-d/2$ to the plane $x+d/2$) and I_{21} (in the opposite direction) [24]. The diffusion flux I_{12} is determined by the number of metal atoms or impurities passing through a unit of surface per unit of time. The number of diffusing atom in each state is determined by the Boltzmann distribution [26]:

$$N_i=\frac{1}{\exp((e_i-\mu)/kT)} \tag{1}$$

where T – temperature, μ is the chemical potential of diffusing atoms, k – Boltzmann's constant.

Having performed calculations for the diffusion flux of atoms, similar to the calculations of the thermionic emission current [26; 27], was find the diffusion flux I_{12} in the direction of the x axis:

$$I_{12}=\frac{2\pi mk^2T^2}{h^3}e^{-(U-\mu_1)/kT} \tag{2}$$

where μ_1 is the chemical potential of diffusing atoms on the side of plane I (Fig. 1), h – Plank constant.

Similarly, was find the diffusion flux I_{21}, where μ_2 is the chemical potential of diffusing atoms on the side of plane II. The total diffusion flux is equal to:

$$Ic=I_{12}-I_{21}=\frac{2\pi mk^2T^2}{h^3}e^{-\frac{w}{kT}}(1-\exp(\Delta\mu/kT)) \tag{3}$$

where μ_2 is the chemical potential of diffusing atoms on the side of plane II, $w=U-\mu_1$, $\Delta\mu=\mu_2-\mu_1$. Chemical potential of diffusing atoms on the side of plane I is taken as the base.

Equation (3) is the most general formula of the statistical model for the diffusion flux of atoms in the crystal lattice [28]. If the diffusion of an element occurs from one phase to another, the chemical potentials of which differ sharply, then it is the exact expression (8) that should be used. If we consider the diffusion of atoms in the single-phase region, then the difference of their chemical potential at the interplanar distance d:$|\Delta\mu|<<kT$, then $\exp(\Delta\mu/kT)\approx$ $\approx 1+\Delta\mu/kT$. According to the average theorem, can find:

$$Ic=\frac{2\pi mkTd}{h^3}e^{-w/kT}\frac{\partial\mu}{\partial x} \tag{4}$$

It is the statistical equation of atoms diffusion in a crystal lattice of a metal. It directly shows that the diffusion flux of atoms directly depends on the gradient of the chemical potential, as it should be in a consistent thermodynamic theory [24; 27]. In this case, equation (4) is the limiting case of equation (3) of the simple statistical model. Using equation (4) allows us to calculate ***ab initio*** the preexponential factor of atoms diffusion in a crystal lattice of a metal [28]. If we further consider the ideal solid solution of the atoms of a substance in a metal, then we can write the following expression [24]:

$$\mu=\mu_0(T)+kT\ln C\text{, whence }\quad\frac{\partial\mu}{\partial x}=\frac{kT}{C}\frac{\partial C}{\partial x} \tag{5}$$

Substituting expression (5) into (4), we find, that the diffusion koefficent in our case is equal:

$$D=\frac{2\pi mk^2T^2d}{h^3}e^{-W_0/kT},W_0=U-\mu_0 \tag{6}$$

and preexponential factor after transformations is [28]:

$$D_0=\frac{2\pi N_e^2m_ak^2T^2d}{h^3N\rho} \tag{7}$$

where N is the Avogadro number (mol^{-1}); N_e is the atomic number of the element (1 for H); m_a is the atomic mass unit (H); ρ is the metall density (g cm^{-3}).

Expression (6) of the developed statistical model significantly differs from the expressions obtained in classical atomic models [16-20]. The interplanar distance d enters into this expression in the first degree. But this formula assumes the dependence of D_0 on the square of the atomic number of the diffusing element and the square of the diffusion temperature. If we compare expression (6) with the classical formula for the diffusion coefficient [16-20]:

$$D=\Delta^2 \nu \tag{8}$$

where Δ is the length of a single jump of an atom during diffusion, ν is the jump frequency, and in formula (6) we put that $d=\Delta$, then for the jump frequency we can find:

$$\nu = \frac{2\pi m k^2 T^2}{h^3 \Delta N \rho} e^{-W_0/kT} \tag{9}$$

We propose to use this expressions (7) and (9) for a more accurate calculation of the hydrogen diffusion coefficients in molecular dynamics (MD) and centroid path-integral molecular dynamics (CMD) [11]. The parameters, calculated in this way, can be called the parameters of the statistical model (SM). The classical expressions for calculating diffusion coefficients does not take into account the Boltzmann distribution of diffusing particles in energy. Therefor the parameters of the statistical model should be used to compare and evaluate the accuracy of both models – MD and CMD.

Results and Discussion

The hydrogen diffusion in α-iron

Let us perform the appropriate calculations for the diffusion of hydrogen in iron and compare them with the experimental data given in [11; 15]. It was shown in [11] that the diffusion of hydrogen in α-iron at high temperatures deviates from the Arrhenius equation, which is an additional indication of the dependence of D0 on the diffusion temperature (Fig. 2).

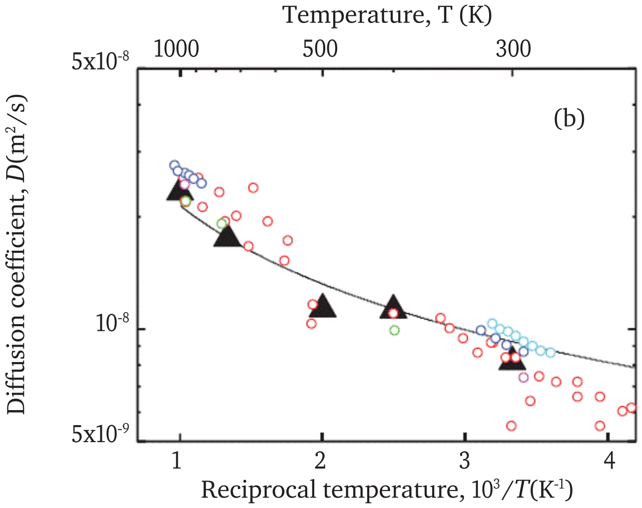

Figure 2. Diffusion coefficients of H in Fe in the temperature range 250-1000 K. The solid triangles represent the CMD results

Source: [11]

Due to the low solubility of H in Fe, it is necessary to carry out experiments at low concentrations of H (<1 ppm under ambient conditions), therefore, even in the case of pure Fe, the experimental information on the diffusion coefficient of H is unreliable compared to the H diffusion in other BCC metals (V, Nb, Ta, etc.) [11].

In the developed statistical model (SM) pre-exponential factor (D_0) we can calculate by the formula [28]:

$$D_0 = 1.14 \cdot \frac{\Delta}{\rho} \cdot T^2 cm^2/S \tag{10}$$

This formula describes well the deviation of the hydrogen diffusion coefficient from the Arrhenius law (Fig. 2).

Table 1. Calculated values for diffusion coefficients (D in 10^{-8} m^2 s^{-1}) of H in α-Fe, together with experimental values

	T=300 K	T=1000 K
Calc. (Classical MD) (Ref. 11)	0.29	2.39
Calc. (CMD) (Ref. 11)	0.83	2.37
Calc. (SM)	0.85	2.78
Expt. (Ref. 15)	–	2.86^b
Expt. (Ref. 29)	0.87^a	2.63^b
Expt. (Ref. 30)	0.74^a	2.45^b

Note: ^{a}At 293 K, ^{b}At 973 K

The results of the molecular dynamics calculations are comparable with the experimental data given in works [11; 15; 29; 30] (Table 1). We can see, that the present SM approach is valid for predicting the absolute values of the diffusion coefficients both below and above the temperature of 500 K. In several experimental studies, the E_a values were practically estimated by the slope of the ln$D$ versus 1/T plot between 300 K and 1000 K [29-31], as listed in Table 2. To compare with these results, we estimate the D values based on SM approximation by formula (6) in the temperature range 300-1000 K; the obtained value of E_a 0.057 eV shows good agreement with experimental and calculated data in the range 0.035-0.081 eV [11; 29-31].

Table 2. Calculated values for an activation energy (E_a) and a preexponential factor (D_0) of H diffusivity in α-Fe in the temperature range of 300-1000 K, together with experimental values

	E_a (eV)	D_0 (10^{-8} m^2 s^{-1})
Calc. (Classical MD) (Ref. 11)	0.081	5.02
Calc. (CMD) (Ref. 11)	0.037	3.23
Calc. (SM) (1000 K)	0.040	4.40
Expt. (Ref. 29) (290 -1040 K)	0.040	4.20
Expt. (Ref. 31) (290 -1040 K)	0.035	3.35
Expt. (Ref. 30) (293 and 973 K)	0.044	4.15

Also, the values of the SM preexponential factor (D_0) are in good agreement with the experimental data [29-31]. Since the classical limit of the migration barrier E_m on a given potential energy surface is set at 0.088 eV, the apparent E_a decreases by 60%, when quantum effects are taken into account [11]. Our approach based on the first principles of a statistical model makes it possible to coherently describe the temperature dependence of the diffusion coefficient H in α-Fe in a wide temperature range from 100 to 1000 K. In particular, at values above 500 K, a clear non-Arrhenius behavior is observed, which arises with allowance for quantum-statistical effects. The results show that statistical effects play a decisive role in the H migration process both at ambient temperature and at higher temperatures.

The hydrogen diffusion in crystal lattice of FCC metals

In metal crystals, hydrogen atoms are in interstitials and in the diffusion process they pass from one interstitial site to another. In FCC lattice, hydrogen can occupy two types of interstitial sites: octahedral and tetrahedral [9]. At the present time, the question of the mechanism of hydrogen diffusion in the crystal lattice of metals remains. Even in a pure crystal, transitions between interstitials of different types are possible, which entails, in particular, the ambiguity of the activation energy of hydrogen diffusion. In addition, as noted in [9], the redistribution of hydrogen atoms in interstitial sites of various types due to changes in external conditions, for example, deformation, can lead to a change in the diffusion parameters. It should be noted that in the statistical model the calculations of the diffusion coefficients fundamentally lead to deviations from the Arrhenius law. This possibility is also shown in other models in particular, the possibility of diffusion jumps of different lengths and the effect of crystal lattice defects [12; 13].

Shown in Figure 3 are possible migration trajectories of a hydrogen atom from one interstitial into the other. Dots on the trajectories are the positions of the hydrogen atom where it possesses the maximum potential energy in the course of migration. When moving between the octahedral pores along a straight-line path (trajectory 1), as is evident in Figure 3, it bumps into a relatively high energy barrier – in the point on the trajectory between two metal atoms along <110>. Trajectory 2 – migration of a hydrogen atom from one octahedral pore into the other across a tetrahedral pore. The migration of hydrogen atoms on trajectory 2 consists of two elementary stages: hydrogen migration from an octahedral pore to a tetrahedral one, and from a tetrahedral into an octahedral pore. As can be seen in Figure 3, at every stage the path and energy barrier smaller than in the first case [9].

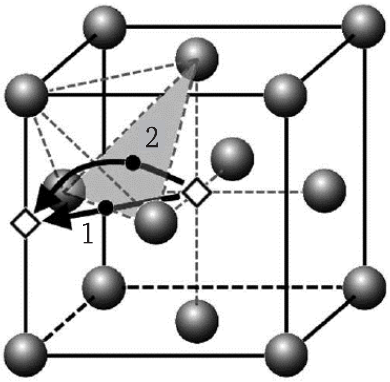

Figure 3. Two possible trajectories of migration of a hydrogen atom from one octahedral pore into the adjacent pore: in a straight line along <110> (1) and across a tetrahedral pore (2). Position of the octahedral pores is indicated by rhombus
Source: [9]

Mechanism 1 seems less possible than mechanism 2 due to the lower height and relative closeness of the energy barrier corresponding to trajectory 2. However it should be taken into account that, firstly, the equilibrium distance between the metal and hydrogen atoms is much less than that between metal atoms (about one and a half times [15]). Secondly, as a result of the thermal oscillations of atoms, the barrier ratio can vary, due to which the probability of realization of the mechanism 1 is nonzero.

Shown in Figure 4 are the curves lnD(T^{-1}) obtained in the work [9] for considered systems Pd–H, Ni–H, Ag–H, Al–H. For the indicated scale on the y-axis, D should be taken in units of mm^2/s (author's note). These curves show a significant deviation from linearity and a ***significant*** scatter of values from the experimental data used in the work [9]. This nonlinearity can be explained by fundamental deviations from the Arrhenius law according to the developed statistical model.

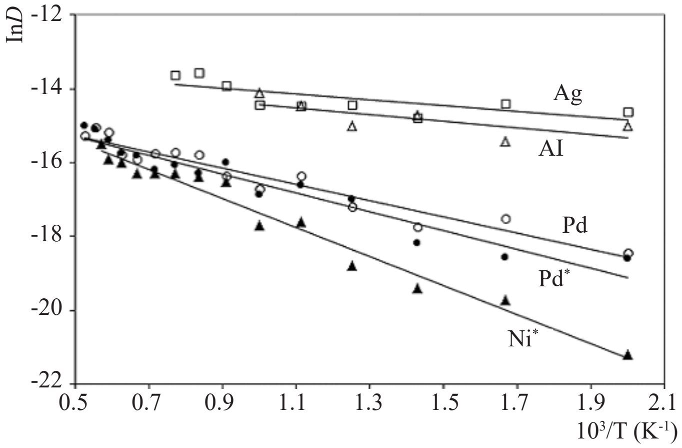

Figure 4. Dependences of lnD on T^{-1} obtained by simulation of hydrogen diffusion in metals Pd, Ni, Ag, Al . The asterisk denotes metals forwhich potentials from [15] were used

Source: [9]

Table 3 lists the values of activation energy and pre-exponential factors estimated in the work [9] and SM and also, for comparison, data from the directory [32].

As can be seen from the table, the values of the activation energy and the pre-exponential factor of the over-barrier diffusion of hydrogen in Pd, Ag, Al, Ni and γ-Fe, obtained in the present work, are better consistent with the experimental data, than the calculations in [9]. The statistical model makes it possible to explain the high values of the preexponential diffusion factor at high temperatures (~10^{-7} m^2s^{-1} – 10^{-6} m^2s^{-1}) due to the coefficient T^2.

Table 3. The migration energy and the pre-exponential factor for hydrogen diffusion in the considered metals obtained using the dynamic method [9] and SM

Metals Parameters	Ag	Al	Pd	Ni	γ-Fe
Calc. (Ref. 9) (E_m (eV)	0.06	0.08	0.23	0.34	–
Calc. (Ref. 9) D_0 10^{-7} (m^2 s^{-1})	4.1	8.1	9.2	15.1	–
Calc. (SM) E_m (eV)	0.30	0.38	0.24	0.45	0.37
Calc. (SM)[a] D_0 10^{-7} (m^2 s^{-1})	2.6	6.8[b]	2.3	3.2	3.5
Expt. (Ref. 32) E_m (eV)	0.32-0.35	0.30-0.48	0.21-0.27	0.35- 0.46	0.35-0.37
Expt. (Ref. 32) D_0 10^{-7} (m^2s^{-1})	8.6-11.2	10-25	1.7-5.3	2.5-7.9	2.9-3.7

Note: [a]At 1200 K, [b]At 900 K

Conclusions

Thus, a simple statistical model of the diffusion of impurity atoms in the crystal lattice of metals is developed in the article. The relationship between the diffusion flux of atoms and the gradient of their chemical potential, as required by nonequilibrium thermodynamics, is obtained from the basic principles of statistical thermodynamics. We propose to use statistical model expressions the preexponential factor and the jump frequency for a more accurate calculation of the hydrogen diffusion in molecular dynamics (MD) and centroid path-integral molecular dynamics (CMD). The calculations performed are compared with the known experimental data on the diffusion of hydrogen atoms in α-iron with a fairly good agreement between the results. Deviations from the Arrhenius law at high temperatures can also be explained by the proposed statistical model. Our approach based on the first principles of a statistical model makes it possible to coherently describe the temperature dependence of the diffusion coefficient H in α-Fe in a wide temperature range from 100 to 1000 K. In particular, at values above 500 K, a clear non-Arrhenius behavior is observed, which arises with allowance for quantum-statistical effects. The results show that statistical effects play a decisive role in the H migration process both at ambient temperature and at higher temperatures.

The values of the activation energy and the pre-exponential factor of the over-barrier diffusion of hydrogen in Pd, Ag, Al, Ni and γ-Fe, obtained in the present work, are better consistent with the experimental data, than the calculations in other works. The statistical model makes it possible to explain the high values of the preexponential diffusion factor at high temperatures (~10^{-7} m^2 s^{-1}– 10^{-6} m^2 s^{-1}) due to the coefficient T^2. Undoubtedly, this model does not take into account many specific factors affecting the diffusion parameters of atoms in a metal, such as the interaction of impurity atoms and metal, the presence of vacancies, quantum tunneling at low temperatures, etc. Further development of this model will allow taking into account the influence of these factors.

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Теоретичні аспекти дифузії водню в металах

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Анотація

Актуальність. Дифузії водню в металах приділено багато уваги і в останні десятиліття було предметом інтенсивного навчання, що пов'язано з практичним інтересом до використання системи метал-водень для низки технологічних застосувань, зокрема створення радіаційно-стійких матеріалів та фільтрів для отримання чистого водню, використання газу Н як вторинного енергоносія та в реакторах термоядерного синтезу. Дифузія Н в сплавах Fe є дуже важливою, оскільки це призводить до інженерних проблем, пов'язаних із водневою крихкістю та деградацією високоміцних сталей, матеріалів реакторів тощо.

Мета. Метою цієї роботи є дослідження механізму дифузії атомів водню в кристалічній решітці металів методом статистичної термодинаміки та розрахунок розширеного рівняння дифузії та передекспоненціального множника для відповідного рівняння Арреніуса.

Методи. Для більш точного розрахунку дифузії водню в молекулярній динаміці (MD) та центроїдній інтегральній молекулярній динаміці (CMD) було запропоновано використовувати статистичні модельні вирази для передекспоненціального коефіцієнту та частоти стрибків атомів.

Результати. Авторський підхід, заснований на перших принципах статистичної моделі, що дає змогу адекватно описати температурну залежність коефіцієнта дифузії Н в α-Fe у широкому діапазоні температур від 100 до 1000 К. Значення енергії активації та передекспоненціального коефіцієнта надбар'єрної дифузії водню в α-Fe, Pd, Ag, Al, Ni та γ-Fe, отримані в цій роботі, добре узгоджуються з експериментальними даними.

Висновки. Результати показують, що статистичні ефекти відіграють вирішальну роль у процесі міграції Н як за температури навколишнього середовища, так і за більш високих температур. Статистична модель дає змогу пояснити високі значення коефіцієнта передекспоненціальної дифузії за високих температур за рахунок коефіцієнта T^2

Ключові слова: статистична модель, дифузія водню, передекспоненційний коефіцієнт, молекулярна динаміка, енергія активації, частота стрибків